# ELECTRONICALLY ACTIVE CYCLOCARBORANE-METAL-ARENE ASSEMBLIES

Final Report

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**13. ABSTRACT** *(Maximum 200 words)*

The designed synthesis of stable, soluble macromolecular complexes incorporating $MC_2B_3$ subunits (in which M is a transition metal) was explored in detail, with emphasis on (1) the efficient preparation of viable building-block molecules such as $Cp^*Co(Et_2C_2B_3H_5)$ ($Cp^* = \eta^5$-$C_5Me_5$); (2) the derivatization and tailoring of these via attachment of substituents (including organic functional groups) to the carborane rings; (3) the construction of multidecker stacks via a novel metal-promoted stacking process; (4) the linkage of stacked sandwiches via coupling, fusion, and other methods; and (5) initial studies on the preparation of electroactive or magnetoactive solid state materials from metallacarborane precursors. The synthesis of novel metallacarborane sandwiches that are direct structural analogues of metallocenes, and mixed-sandwich salts of the type $Cp_2M^+$ $[(Et_2C_2B_n)_2M']^-$ in which M and M′ are transition metals was also achieved. Detailed studies of the molecular and electronic structures of many of the above systems were conducted via NMR, ESR, X-ray crystallography, and electrochemical methods.

**14. SUBJECT TERMS**

carboranes; metallacarboranes; cobaltacarboranes; metal-arene complexes; sandwich complexes; multidecker sandwich complexes; macromolecules; organometallic polymers

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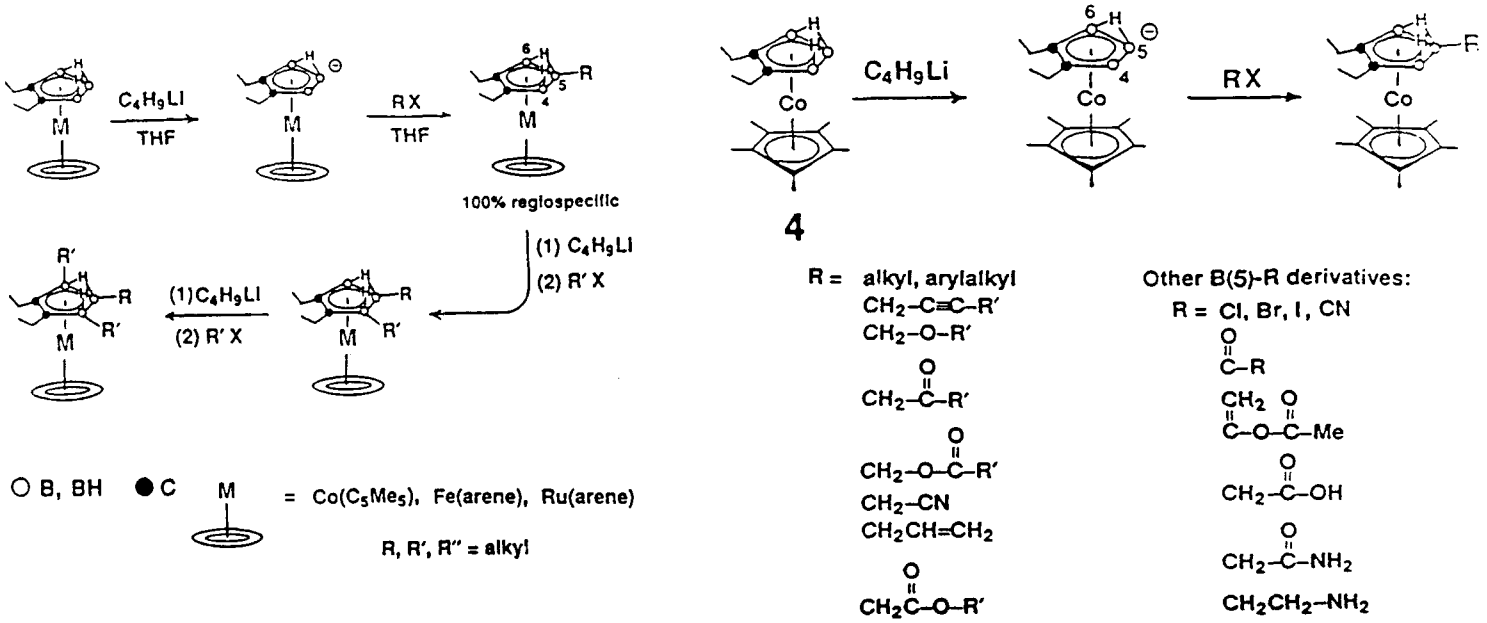
## I. Statement of Problem

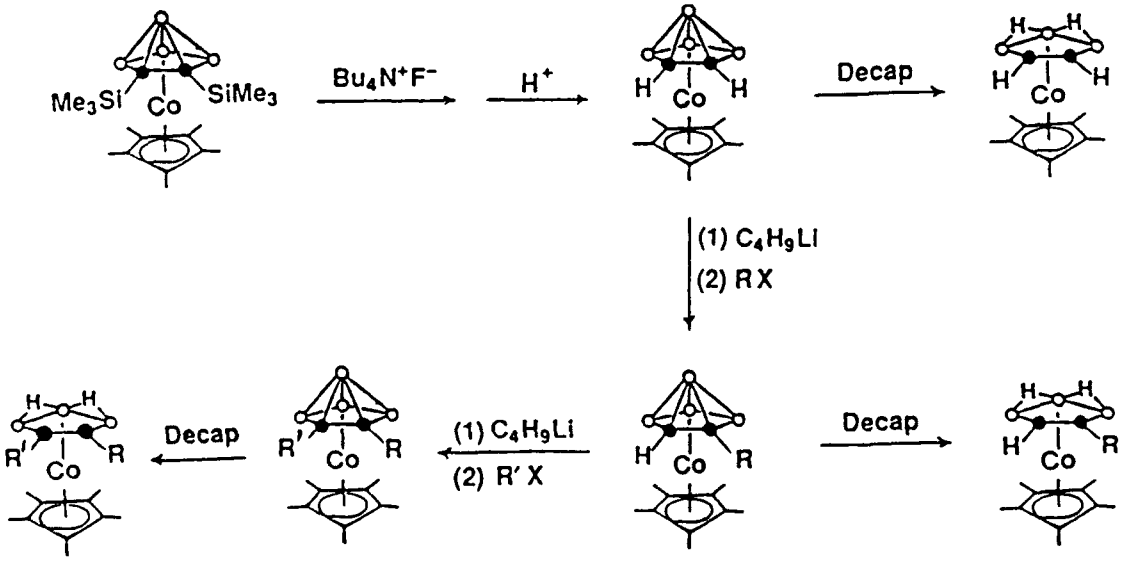
This research was concerned with the development of designed synthetic routes to stable multi-metal stacked and linked sandwich complexes that are potential precursors to electroactive or magnetoactive polymers or solid-state materials, as well as studies of their electronic and molecular structures, physical properties, and chemical reactivity.

## II. Summary of Important Results

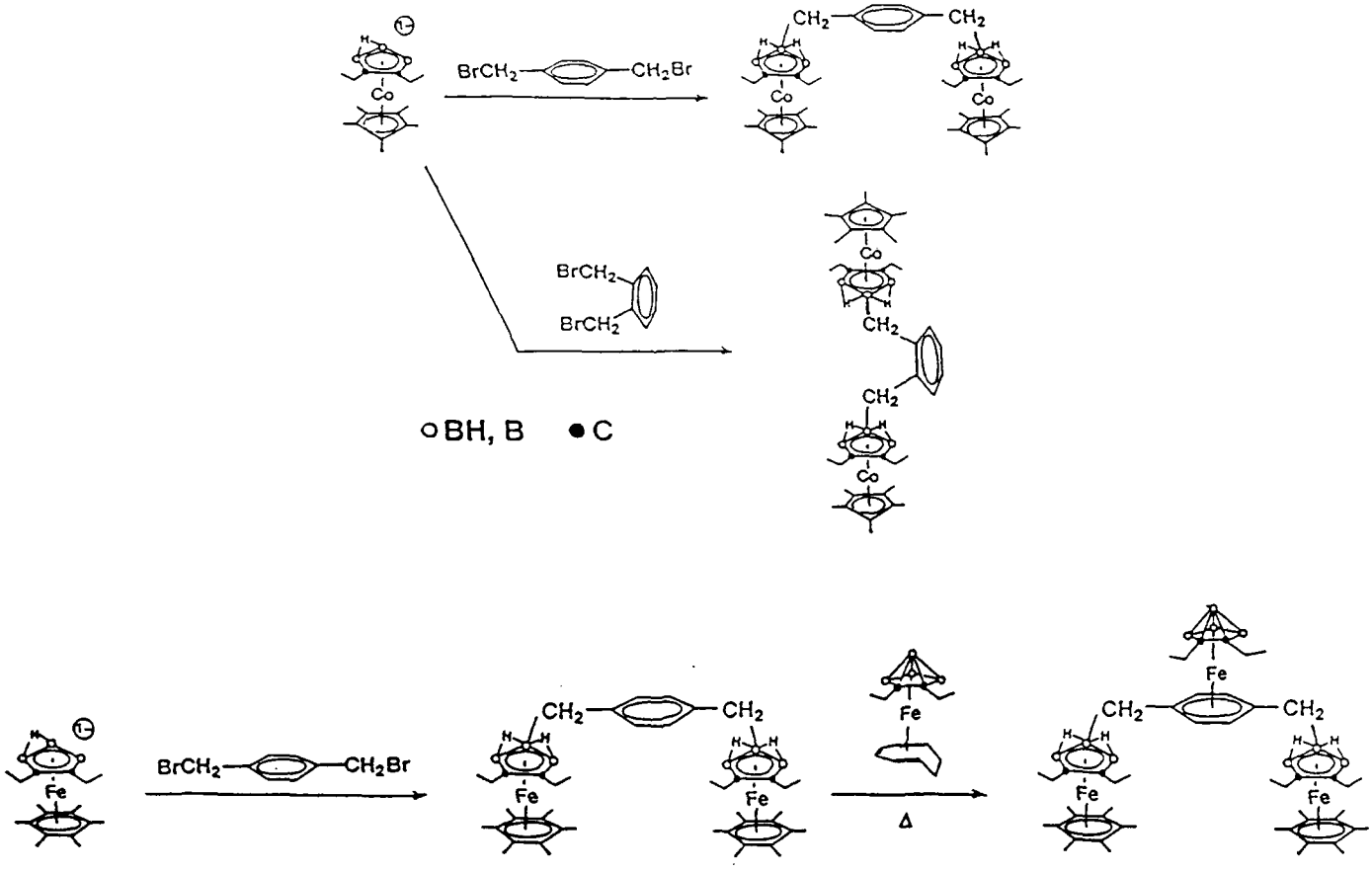
***1. Controlled derivitization of nido-LM($RR'C_2B_3H_5$) synthons (LM = Cp*Co, CpCo, (arene)Fe, or (arene)Ru).*** Procedures we developed earlier for alkylating the $C_2B_3$ rings in these complexes have been extended to generate a wide variety of organic and halogen derivatives, primarily of the cobalt species $Cp^*Co(Et_2C_2B_3H_5)$.



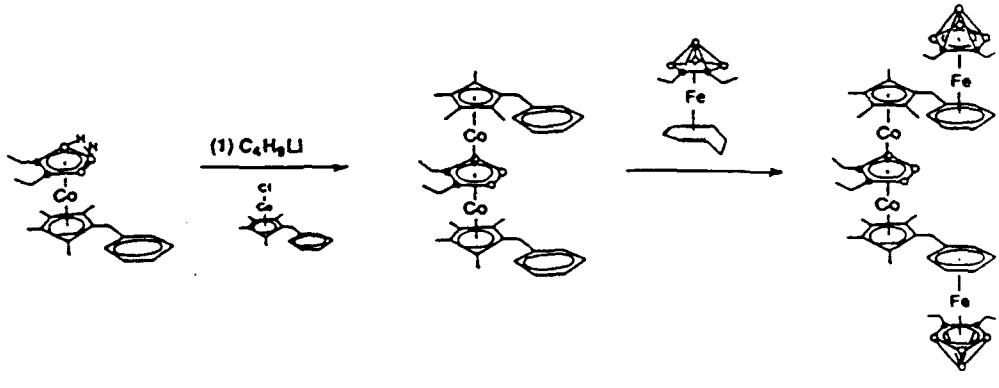

A method for selective derivatization at the cage *carbon* atoms via desilylation of C-trimethylsilyl closo clusters was found, that surprisingly involves *catalytic* cleavage of the C-Si bonds, apparently unprecedented, via the action of $(C_4H_9)_4N^+F^-$ (TBAF). The cage C-H protons in the parent complex are acidic and can be replaced by organic substituents as shown.



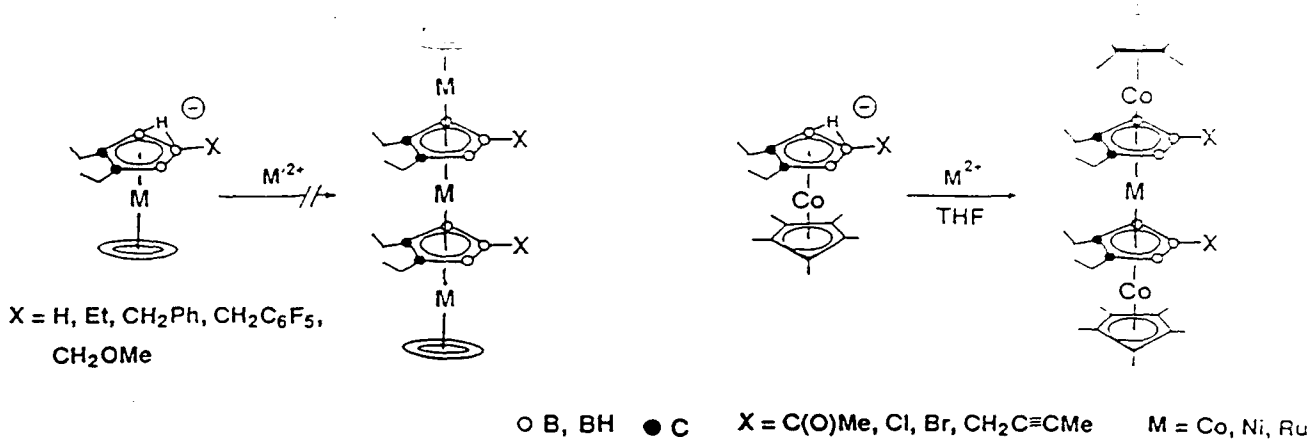
*2. Directed Synthesis of Linked Sandwich Complexes.* The above methods for attaching functional groups regioselectively on the $C_2B_3$ ring were exploited to prepare hydrocarbon-linked oligomers via reactions of organic dihalides:



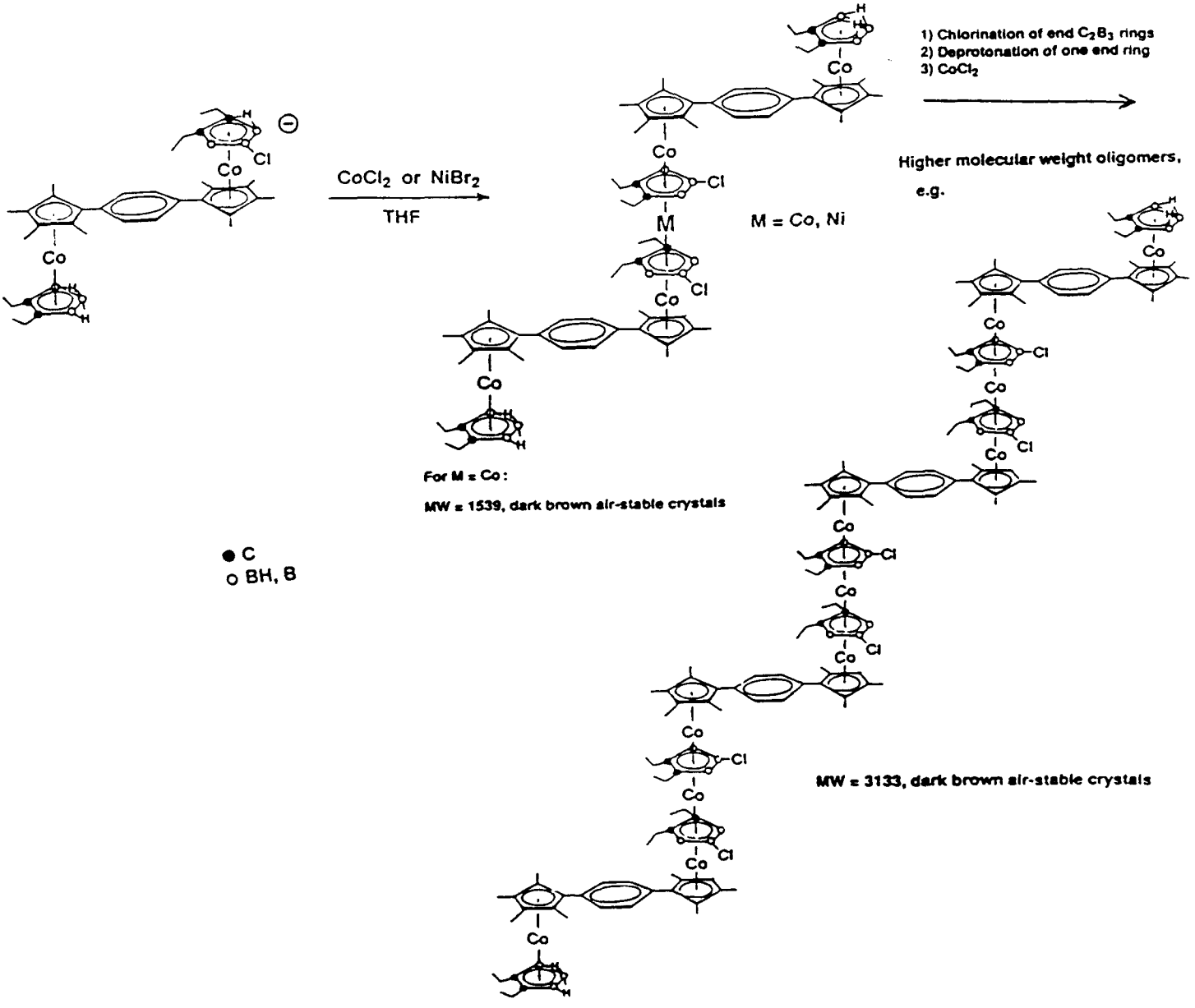

Alternatively, we have also shown that polycyclic hydrocarbon ligands can be employed to link multisandwich species via metal-$C_n$ ring coordination:




*3. Synthesis of Tetradecker Sandwich Complexes via Metal-Promoted Stacking of Double-Decker Synthons.* Although we had previously tried this approach unsuccessfully, in 1991 we found that tetradecker formation via stacking of metallacarborane double-decker anions can be achieved when the "middle" hydrogen [B(5)-H] is replaced by a suitable substituent, *e.g.*, Cl, Br, acetyl, methyl; the parent (X = H) complex can also be isolated provided exposure to air and silica are avoided. The tetradecker sandwich geometry has been confirmed by X-ray structural studies on several Co-Co-Co, Co-Ni-Co, and Co-Ru-Co complexes.

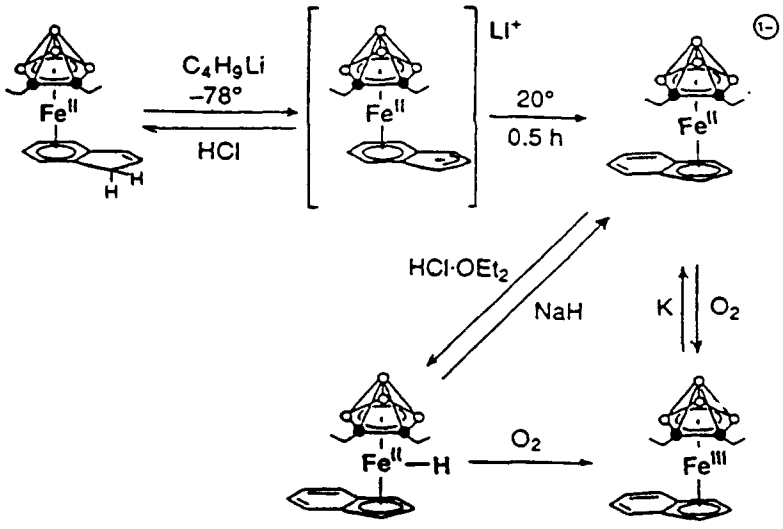



***4. Designed Synthesis of Multi-Tetradecker Sandwich Oligomers and Polymers.*** The tetradecker stacking reaction has been employed to prepare a number of macromolecular polyarene-linked complexes such as those illustrated (the 5-cobalt species has been confirmed by X-ray crystallography). Although the phenylene-linked systems are unlikely to have delocalization of electrons between the stacks, we have recently prepared analogous systems employing fulvalene [$(C_5H_4)_2$] as the linking unit, and the prospects for delocalization (hence conductivity) are good.



*5. Studies of Electronic Structures and Properties* Multinuclear NMR ($^{1}H$, $^{11}B$, $^{13}C$), ESR, cyclic voltammetry, Mössbauer, magnetic susceptibility studies, and X-ray crystallographic structure determinations have been employed to probe the systems described above, in some cases in collaboration with other research groups. These complexes undergo multiple oxidation and reduction processes without degradation or irreversible structural change, in contrast to many hydrocarbon-metal sandwich species (most of which, other than ferrocene, tend toward oxidative instability).

The redox stability of small-carborane stabilized metal sandwich complexes is well documented, as for example, in the reversible oxidation of $Fe^{II}$-arenes (otherwise virtually unknown) and in the ring-migration of Fe on indenyl-ferracarborane sandwiches.




*6. Coupling and Fusion of Metallacarborane Substrate Molecules.* As outlined in several recent Progress Reports, a number of modes of coupling and linkage of small cobaltacarboranes (some of them novel) have been found in recent work. In some cases the reactions involved are analogous to classical procedures (e.g. Wurtz coupling of halo-substituted species), while in others the processes involve metal-promoted oxidative fusion and are similar to fusions discovered earlier in our group.

## III. Publications produced under this Contract


J. H. Davis, Jr., M. D. Attwood, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 15. Regiospecific B-Alkylation of (arene)M($Et_2C_2B_3H_5$)(M = Fe, Ru) and ($C_5Me_5$)Co($Et_2C_2B_3H_5$) Sandwich Complexes," Organometallics, **1990**, 9, 1171.

M. D. Attwood, J. H. Davis, Jr., and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 16. Directed Synthesis of Arene-Linked Metal Sandwich Complexes via Controlled Substitution on Boron," Organometallics, **1990**, 9, 1177.

J. H. Davis, Jr., M. A. Benvenuto, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 18. $\eta^6$, $\eta^5$-Benzyltetramethylcyclopentadieneide(1-) as a Bridging Ligand in Multilevel Iron-Cobalt Sandwich Complexes," Inorg. Chem. **1991**, 30, 1765.


continued

K. W. Piepgrass, J. H. Davis, Jr., M. Sabat, and R. N. Grimes, "Unusual Organic Chemistry on a Metallacarborane Substrate: Formation of a B-Vinyl Ester from Acetyl Chloride", J. Am. Chem. Soc., **1991**, 113, 680.

K. W. Piepgrass, J. H. Davis, Jr., M. Sabat, and R. N. Grimes, "Electronic Control of Metallacarborane Stacking Reactions. Directed Synthesis of $Cp^*Co(C_2B_3)M(C_2B_3)CoCp^*$ Tetradecker Sandwiches", J. Am. Chem. Soc., **1991**, 113, 681.

R. N. Grimes, "Small Carboranes as Building Blocks in Designed Organometallic Synthesis," Pure Appl. Chem., **1991**, 63, 369.

A. Fessenbecker, M. Stephan, R. N. Grimes, H. Pritzkow, U. Zenneck, and W. Siebert, "Organotransition-Metal Metallacarboranes. 19. Indenyliron(II) and -iron(III) Complexes and Related Species. $\eta^6 \rightarrow \eta^5$ Haptotropic Rearrangement, Electrochemistry, and Polyhedral Expansion of (Arene)Fe($Et_2C_2B_4H_4$) Clusters", J. Am. Chem. Soc., **1991**, 113, 3061.

M. A. Benvenuto and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 20. $Bu_4N^+F^-$ Fluoride-Catalyzed C-Si Bond Cleavage in $Cp^*Co(Me_3Si)_2C_2B_4H_4$. Synthesis of Parent $Cp^*CoC_2B_4H_6$ and Conversion to C-Substituted $Cp^*CoRR'C_2B_4H_4$ Derivatives", Inorg. Chem. **1991**, 30, 2836.

R. N. Grimes, "Cyclocarborane-Stabilized Multidecker/Multicluster Sandwich Compounds and Linked Molecular Systems", in Electron-Deficient Boron and Carbon Clusters, G. A. Olah, K. Wade, and R. E. Williams, Eds., John Wiley & Sons, Inc., New York, **1991**, Chapter 11, pp 261-285.

M. Stephan, J. H. Davis, Jr., X. Meng, K. J. Chase, Jan Hauss, U. Zenneck, H. Pritzkow, W. Siebert, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 25. Redox Chemistry and Electronic Studies of Mono- and Dinuclear Iron(II)/Iron(III) Sandwich Complexes", J. Am. Chem. Soc. **1992**, 114, 5214.

K. W. Piepgrass and R. N. Grimes, "$(C_5Me_5)Co(Et_2C_2B_3H_4$-R) Metallacarborane Sandwich Complexes as Versatile Synthons. Introduction of Organomethyl Functional Groups at Boron", Organometallics **1992**, 11, 2397.

K. W. Piepgrass, K. E. Stockman, M. Sabat, and R. N. Grimes, "$(C_5Me_5)Co(Et_2C_2B_3H_4$-R) Metallacarborane Sandwich Complexes as Versatile Synthons. Introduction of Electron-Withdrawing Substituents", Organometallics **1992**, 11, 2404.

R. N. Grimes, "Boron-Carbon Ring Ligands in Organometallic Synthesis", Chem. Rev. **1992**, 92, 251.

M. A. Benvenuto and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 28. Controlled Substitution at Cage Carbon Atoms in $CoC_2B_4$ Clusters. Linkage of Bis(cobaltacarborane) Sandwich Complexes via Carbon-Bound Bridging Groups", Inorg. Chem., in press.

M. A. Benvenuto, M. Sabat, and R. N. Grimes, "Organotransition-Metal Metallacarboranes. 29. Synthesis of Selectively C- and B-Substituted Double- and Triple-Decker Sandwiches. $(\eta^5$-$C_5Me_5)Co^{III}(\eta^5$-$R_2C_2B_3R'_3H_2)$ Cobalticinium Analogues", Inorg. Chem., in press.

continued

K. W. Piepgrass, Xiangsheng Meng, M. Hölscher, M. Sabat, and R. N. Grimes, "Tetradecker Metallacarborane Sandwiches: Synthesis via Double-Decker Stacking and Structural Characterization of Co-Co-Co, Co-Ni-Co, and Co-Ru-Co Complexes", submitted for publication.

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